2004 DOE Hydrogen, Fuel Cells, & Infrastructure Technologies Program Review

Development of Polybenzimidazole-based, High Temperature Membrane and Electrode Assemblies for Stationary and Automotive Applications

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PROJECT OVERVIEW AND OBJECTIVES TO DATE

To identify and demonstrate an MEA based on a high-temperature polybenzimidazole (PBI) membrane that can achieve the performance, durability, and cost targets required for both stationary and automotive fuel cell applications.

❖ Complete initial screening of potential PBI-based chemistries and structures and downselect top 5 - 10 candidate materials based on chemical and physical properties.

❖ Initiate rapid screening of candidate PBI materials in 50 cm2 MEAs.

❖ Initiate detailed electrochemical characterization of MEAs made with selected PBI polymers.

❖ Initiate evaluation of low cost acid-absorbing materials for phosphoric acid management within the system.

❖ Initiate design and development of bipolar plates with PBI-specific flow fields.

❖ Initiate development of a PBI membrane-based MEA with advanced electrode structures providing high catalyst utilization and performance exceeding that of Nafion.

DOE TECHNICAL BARRIERS

❖ O. Stack Material and Manufacturing Cost

❖ P. Durability

DOE TECHNICAL TARGETS

❖ Applicable to both automotive and stationary fuel cell systems

❖ Operating temperature > 120°C

❖ Operating pressure from 1 – 3 atm (abs)

❖ Membrane area specific resistance < 0.1 Ω-cm^2

❖ Gas crossover < 1%

❖ MEA manufacturing process scalable from 50 to at least 250 cm^2

❖ Automotive MEA cost target of < $10/kW at a volume of 500,000 fuel cell stacks per year

❖ Stationary system cost target of < $1500/kW at 1,000 fuel cell stacks per year

❖ Projected design lifetime > 40,000 hours

TEAM

❖ Plug Power Inc.
- Prime contractor
- Membrane and membrane electrode assembly (MEA) characterization
- PBI-specific hardware development

❖ Rensselaer Polytechnic Institute
- Membrane formulation, evaluation, and selection
- Membrane processing parameter optimization

❖ Albany NanoTech, University at Albany, SUNY
- Nanofabricated electrodes

❖ Celanese Ventures GmbH
- Membrane and MEA production
- MEA cost modeling

PROGRAM BUDGET

CY	Total $		DOE $		Contractor $	
2003 Actual	$	509,578	$	407,662	$	101,916
2004	$	3,352,106	$	2,681,685	$	670,421
2005	$	2,268,780	$	1,815,024	$	453,756
2006	$	1,163,799	$	931,039	$	232,760
Total	$	7,294,263	$	5,835,410	$	1,458,853

CY 2003 shortfall of $600K moved to 2004 - 06.

APPROACH - Focus 1
Screening of candidate polymers and membrane fabrication processes

❖ Task 1: Polymer screening and preliminary evaluation
   • Identify and standardize chemical, physical, and mechanical test methods
   • Identify potential PBI-based polymers for evaluation
   • Characterize polymers by molecular weight, phosphoric acid content, proton conductivity, and film mechanical strength
   • Identify 5 - 10 lead candidate materials for further evaluation

❖ Task 2: Detailed polymer characterization
   • Characterize the structure and properties of polymer films
   • Determine the relationships between polymer structure and membrane properties
   • Develop processes to produce larger quantities of material (~1 L)
   • Identify 1 - 3 candidates for continued evaluation

❖ Task 3: Low-cost membrane formation techniques
   • Identify the key parameters for membrane formation
   • Define the optimum processing conditions for membrane formation (e.g., polymer concentration, temperature, casting speed, humidity levels)

❖ Task 4: Membrane scale-up
   • Demonstrate ability to produce membranes in sufficient quantities to meet program needs.

APPROACH - Focus 2
MEA Characterization

❖ Task 5: 10-50 cm^2 MEA screening
  - Fabricate MEAs from membranes made from candidate and standard gas diffusion layers
  - Test at limited conditions - 120^oC and 160^oC, reformate with 50 ppm CO and 10,000 ppm CO
  - Operate for 10 hours
  - Combine MEA screening performance with Task 1 property screening data for downselection

❖ Task 6: 50 cm^2 MEA evaluation
  - Conducted detailed parametric studies of MEAs made with membranes with acceptable physical and electrochemical properties
  - Operate cells at multiple temperatures between 100 and 200^oC, pressures between 1 and 3 atm (abs), hydrogen/air and reformate/air, multiple CO concentrations in reformate.
  - Combine MEA performance data with property data obtained in Task 2 for selection of final candidate materials.

❖ Task 7: 440 cm^2 MEA test in short stack
  - Evaluate the final membrane material(s) in short stack

❖ Task 8: Long-term MEA performance characterization
  - Fabricate MEAs for testing in a 50 cm^2 single cell, in a 440 cm^2 single cell, and in a 440 cm^2 short stack
  - Operate cells/stack for at least 1,000 hours under expected operating conditions
  - Determine cell degradation rate and degradation mechanism

APPROACH - Focus 3
Hardware Development and Demonstration

❖ Task 9: Acid management
- Characterize the acid-absorbing capacity of several candidate materials under different temperature and pressure conditions.
- Select the optimum material and design an enclosure with at least two-years of acid-absorbing capacity.

❖ Task 10: PBI-specific flow field design
- Conduct CFD simulations to determine the optimum flow field geometry for PBI membranes
- Confirm simulation results with 50 cm^2 cells
- Design prototypical sized plates incorporating lessons learned
- Design sealing mechanism that provides adequate sealing with minimal compression.

❖ Task 11: Electrode development and performance improvement
- Develop a model of phosphoric acid electrodes to determine optimum electrode properties
- Characterize the effects of electrode structure on performance.
- Develop a nanostructured electrode that maximizes catalyst utilization.

❖ Task 12: Cost assessment
- Build a cost projection model that incorporates data obtained during this program - membrane composition, membrane and MEA manufacturing processes, MEA performance, degradation rates, etc.
- Project MEA costs based on anticipated market demand
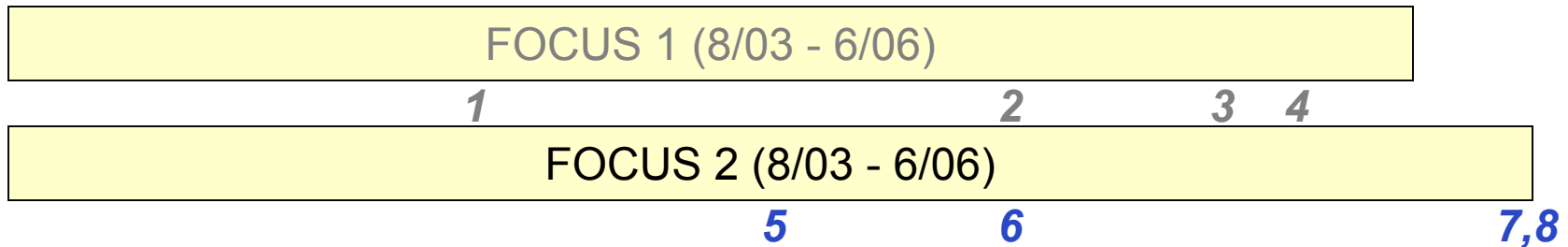
SCHEDULE / MILESTONES

FOCUS 1 (8/03 - 6/06)

1   *2*   *3* *4*

Focus 1 - Polymer and membrane screening and fabrication

1   Initial list of 5 - 10 candidate materials

2   List of ~3 final candidate materials

3   Membrane fabrication process parameters defined

4   Full-size MEAs from scaled up process delivered for testing

SCHEDULE / MILESTONES

FOCUS 1 (8/03 - 6/06)

1   2   3   4

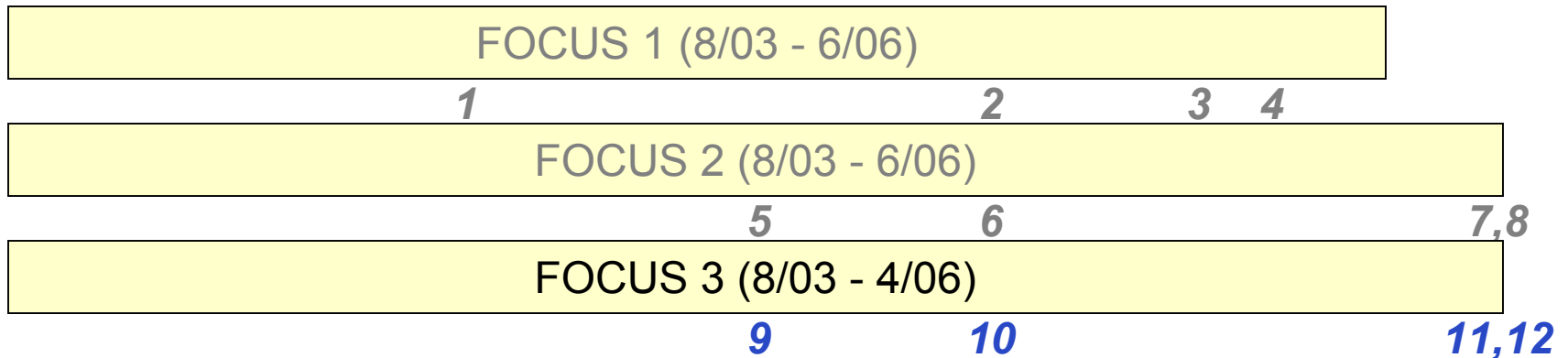| FOCUS 2 (8/03 - 6/06) |
|---|

5   6   7,8

Focus 1 - Polymer and membrane screening and fabrication

  1   *Initial list of 5 - 10 candidate materials*
  2   *List of ~3 final candidate materials*
  3   *Membrane fabrication process parameters defined*
  4   *Full-size MEAs from scaled up process delivered for testing*

Focus 2 - MEA characterization

  5   *Initial MEA screening complete*
  6   *MEA electrochemical property data*
  7   *Full-sized MEA testing in short stack completed*
  8   *MEA degradation mechanism(s) and rate identified*

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SCHEDULE / MILESTONES

FOCUS 1 (8/03 - 6/06)

1	*2*	*3*	*4*

FOCUS 2 (8/03 - 6/06)

5	*6*	*7,8*

FOCUS 3 (8/03 - 4/06)

9	*10*	*11,12*

Focus 1 - Polymer and membrane screening and fabrication

- *1   Initial list of 5 - 10 candidate materials*
- *2   List of ~3 final candidate materials*
- *3   Membrane fabrication process parameters defined*
- *4   Full-size MEAs from scaled up process delivered for testing*

Focus 2 - MEA characterization

- *5   Initial MEA screening complete*
- *6   MEA electrochemical property data*
- *7   Full-sized MEA testing in short stack completed*
- *8   MEA degradation mechanism(s) and rate identified*

Focus 3 - Hardware development and demonstration

- *9   Absorbent material and enclosure for acid management verified*
- *10   Optimized flow field designed and verified*
- *11   Improved electrodes demonstrated*
- *12   MEA cost model and cost projections completed*

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PROJECT SAFETY

❖ Full-time EHS manager provides oversight, training, and guidance.

❖ Annual laboratory safety training of all personnel and new employees.

❖ Laboratories designed to meet OSHA/NFPA Class I, Div. 2 requirements.

❖ Standard operating procedures prepared and maintained for all test and laboratory equipment.

❖ Safety reviews of all test systems and laboratories prior to operation.

❖ Chemical inventory and storage records audited annually.

❖ Use of an Open Safety Items tracking system to schedule and ensure closure of any identified safety issue.

❖ All products subjected to industry certifications as appropriate (e.g., UL, CSA, NEBS, and CE).

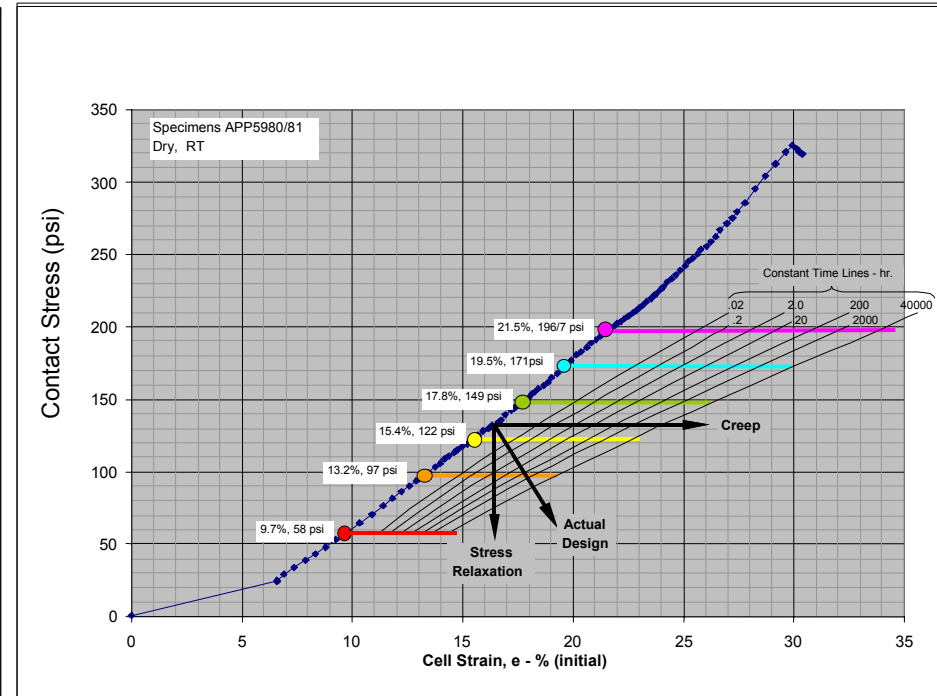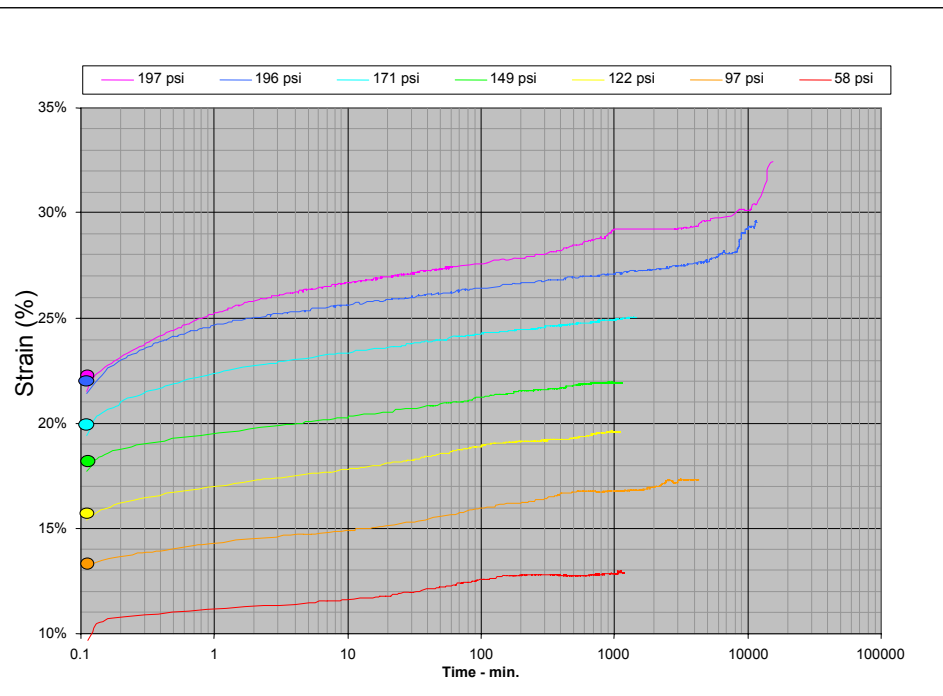# TECHNICAL ACCOMPLISHMENTS
Polymer Screening (Task 1)

Composition	IV (dL/g)	Polymer Content (wt%)	Acid Content (wt%)	Water Content (wt%)	n(H_3PO_4)/n(PBI)	Conductivity (S/cm) at 160° C
1	2.9	6	65	30	38	0.18
2	4.1	4	72	24	49	0.18
3	0.8	15	60	25	46	0.2 (*)
4	1.7	6	80	14	42	0.2 (*)
5	1.2	21	63	16	10	0.1

(*) Measured at 140°C; membrane melted at 160°C.

- First 5 PBI compositions identified, each with a unique chemical structure.

- Membranes were made from each of the first 5 polymers.

- High molecular weight polymers were obtained (typical plant-grade PBI inherent viscosity is 0.8 - 1.0 dL/g).

- All of the phosphoric acid contents obtained were greater than previously reported for PBI materials.

TECHNICAL ACCOMPLISHMENTS
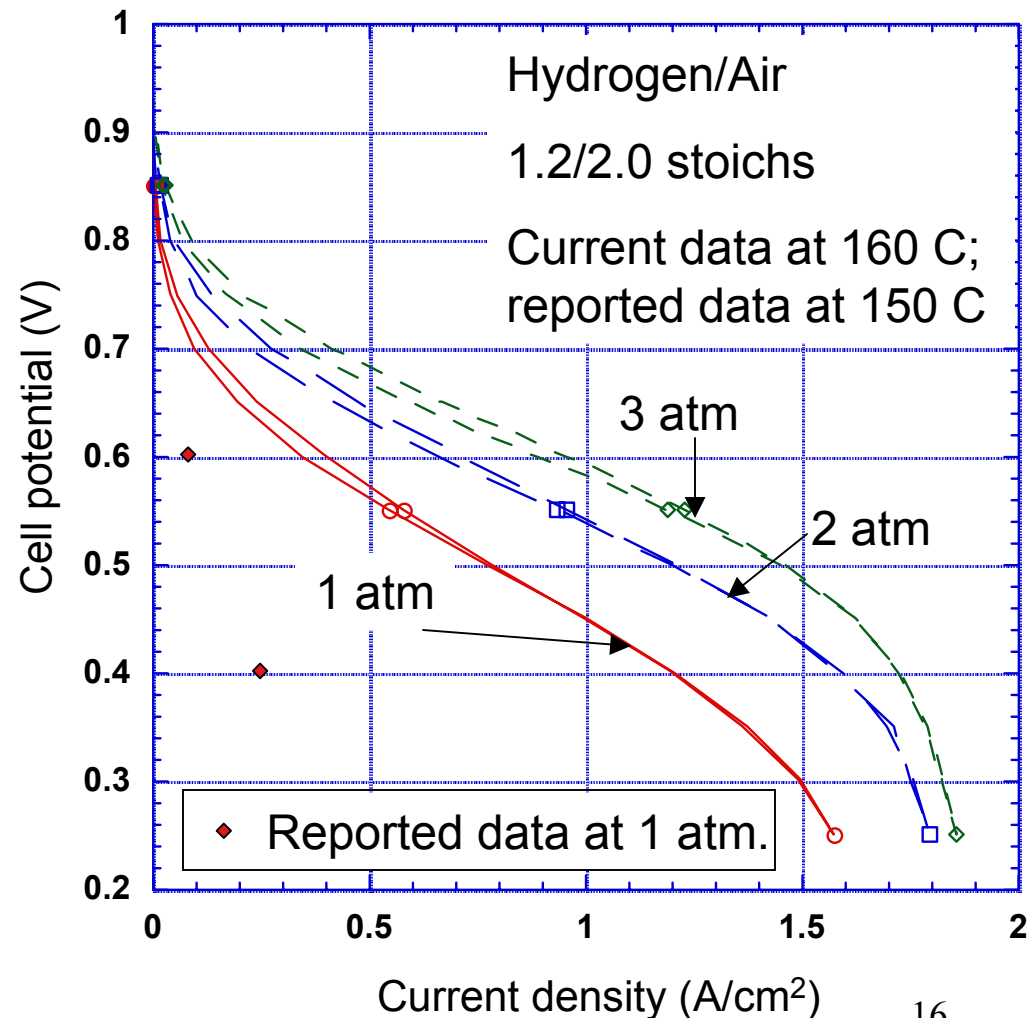## Membrane Characterization (Task 2)

- ❖ Membranes exhibit a high initial rate of creep under constant load.
- ❖ This behavior has significant ramifications for stack design.
- ❖ Membrane behavior will affect the design of stack seals, end hardware, and plates.
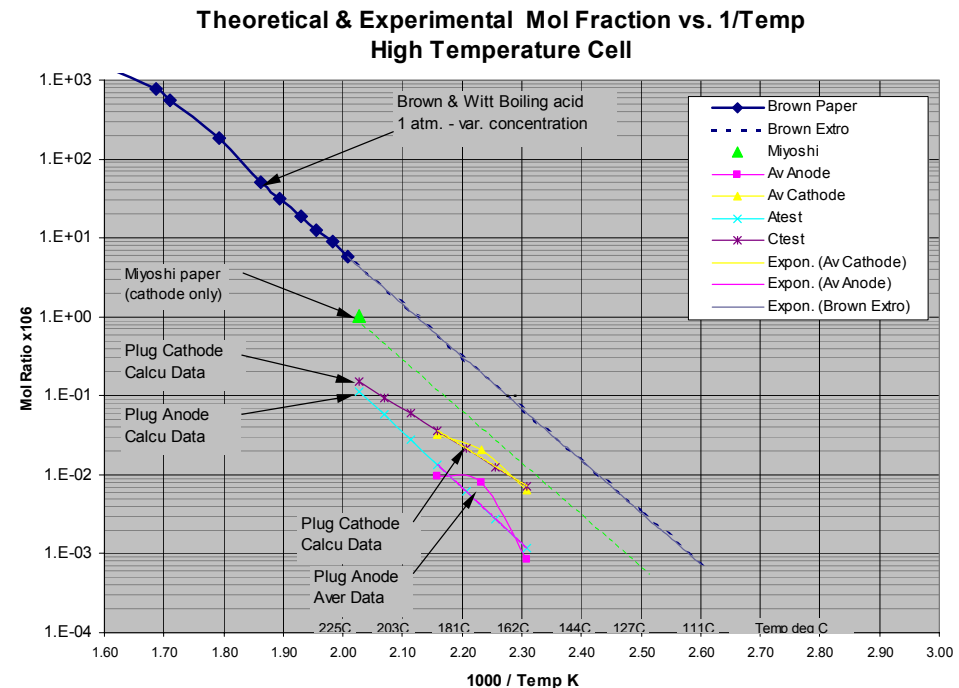
TECHNICAL ACCOMPLISHMENTS
MEA Screening (Task 5)

- MEA performance exceeds previously reported polarization data.

- Measured pressure effect: ΔV (mV) = 75 log(P_2/P_1)

- PAFC theoretical value: ΔV (mV) = 146 log(P_2/P_1)

Hydrogen/Air

1.2/2.0 stoichs

Current data at 160 C; reported data at 150 C

3 atm

2 atm

1 atm

♦ Reported data at 1 atm.

Cell potential (V)

Current density (A/cm^2)

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TECHNICAL ACCOMPLISHMENTS
Acid Management (Task 9)

❖ Identified the mechanisms for acid transport in and from a cell:

  ❖ Diffusion

  ❖ Capillary transport

  ❖ Compression

  ❖ Evaporation

❖ Steady state phosphoric acid evaporation losses were studied on the current membrane and found to be less than theoretical.

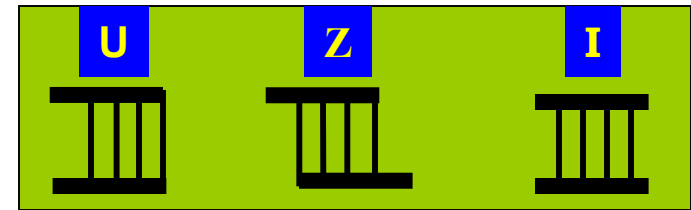❖ Isolating a cell from test station prevents phosphoric acid loss during startup and shutdown .

Theoretical & Experimental Mol Fraction vs. 1/Temp High Temperature Cell

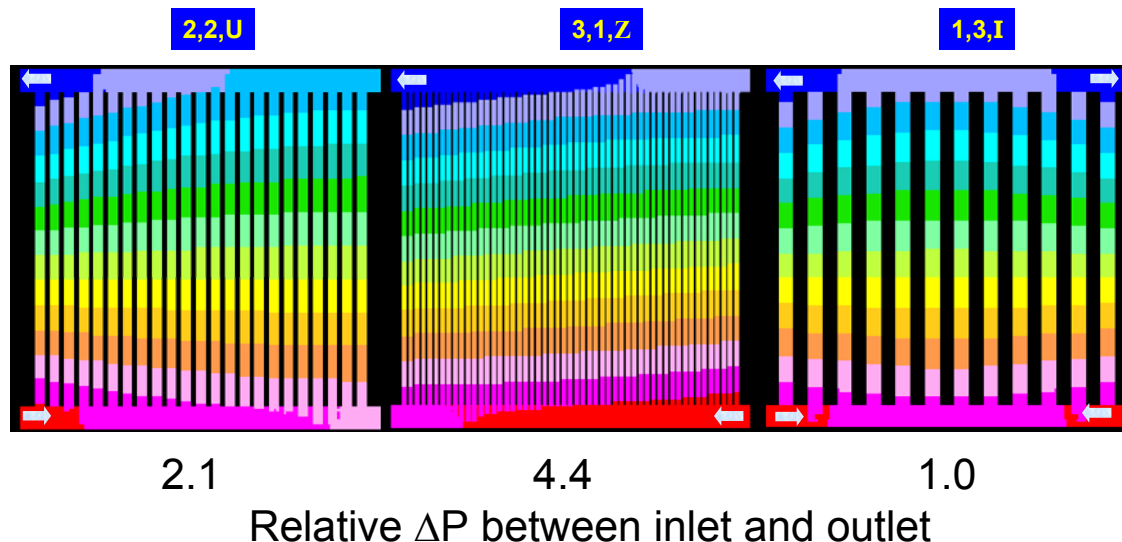*Projected cell life is 40,000 hours with these loss rates.*

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TECHNICAL ACCOMPLISHMENTS
Flow Field Optimization (Task 10)

Experiment number	Channel/land ratio	Relative channel width	Relative flow area	Manifold configuration
1	1.0	1.0	1.0	U
2	1.0	2.0	2.0	Z
3	1.0	3.0	3.0	I
4	2.0	1.0	2.0	I
5	2.0	2.0	3.0	U
6	2.0	3.0	1.0	Z
7	3.0	1.0	3.0	Z
8	3.0	2.0	1.0	I
9	3.0	3.0	2.0	U

- ❖ Flow uniformity decreases as flow area increases.
- ❖ Channel width does not impact flow distribution.
- ❖ Channel-to-land ratio does not impact flow distribution.
- ❖ Manifold size and configuration strongly impact flow uniformity and pressure distribution.

Pressure distribution - Relative flow area = 3.0

2.1   4.4   1.0

Relative ΔP between inlet and outlet

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KNOWLEDGE AND TECHNOLOGY TRANSFER ACTIVITIES

❖ Elter, John, "IPHE as Facilitator of Hydrogen and Fuel Cell Markets for Stationary Applications," Presentation to the International Partnership for a Hydrogen Economy, Washington, DC, November 2003.

❖ "NextGenCell - The next generation of stationary fuel cells," Expression of Interest submitted to the European Commission, Plug Power Inc., Vaillant GmbH, and Celanese Ventures GmbH, March 2004.

❖ Benicewicz, Brian, "PBI Membranes and MEAs for Stationary and Automotive Applications," Presentation to Los Alamos National Laboratory, Los Alamos, New Mexico, March 2004.

❖ Benicewicz, Brian, "PBI Membranes and MEAs for Stationary and Automotive Applications," Presentation to University of New Mexico, Albuquerque, New Mexico, March 2004.

FUTURE WORK

❖ <u>Remainder of 2004</u>:

- Prepare additional polymers and membrane materials for testing.
- Test and evaluate lead candidate materials in 50 cm^2 single cells.
- Characterize the physical and mechanical properties of the lead candidate materials.
- Develop a concept to manage acid loss.
- Design a prototypical size PBI-specific flow field.

FUTURE WORK

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- Characterize the physical and mechanical properties of the lead candidate materials.
- Develop a concept to manage acid loss.
- Design a prototypical size PBI-specific flow field.

❖ <u>2005 - 2006</u>:

- Downselect to the 1 - 3 polymers that show highest likelihood of achieving the program performance, reliability, and cost goals.
- Complete an in-depth parametric characterization of final candidate materials.
- Complete and verify an optimized flow field design in a short stack.
- Complete and demonstrate appropriate acid management hardware.
- Determine and understand the MEA degradation rate in a short stack.
- Demonstrate a PBI-based MEA that meets or exceeds program goals in a short stack.
- Develop and exercise a model to project MEA cost at high volumes.

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